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SYNTHESIS AND PHYSICAL / ELECTROCHEMICAL CHARACTERISATION OF NITROGEN - DOPED CARBON / ACTIVATED CARBONS AS AN EXCELLENT ELECTRODE MATERIAL FOR ELECTROCHEMICAL CAPACITOR APPLICATIONS

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ABSTRACT

Highly porous nitrogen doped carbon / activated carbons were synthesised through polycondensation of resorcinol (R) and formaldehyde (F) where nitrogen was incorporated into polymer matrix using melamine as nitrogen source. N-doped carbon / activated carbons were characterised for their physical structure and their electrochemical performance was analysed when used as electroactive material in electrochemical capacitor cell.

Porous parameters of N-doped carbon / activated carbons was characterised by nitrogen adsorption-desorption measurements. There was no significant change in average pore size however enormous increase in specific surface area from $841\text{m}^2\text{g}^{-1}$ to $1372\text{m}^2\text{g}^{-1}$ was observed after activation processes at elevated temperature under CO_2 . N-doped carbon / activated carbons were characterised electrochemically using cyclic voltammetry measurements which showed nitrogen enriched activated carbons (mRFCA) exhibited the improved specific capacitance of up to 289Fg^{-1} as compare to 208Fg^{-1} of nitrogen enriched carbon (mRFC) at the scan rate of 5mVs^{-1} using 6M KOH electrolyte. Improved capacitive performance of mRFCA can be attributed to the combined effect of the increased specific surface area and extra pseudocapacitance generated due to nitrogen- containing functionalities incorporated into the bulk of the electroactive material.

Keywords: Electrode material, Functional groups, Nitrogen enriched activated carbons, Cyclic voltammetry, Capacitive performance

1 INTRODUCTION

Electrochemical capacitors (ECs), also known as ultra-capacitors or supercapacitors, retain properties such as long cycle life, excellent safety, high power density and high efficiency when compared with other electrical energy storage devices [1, 2]. ECs have been widely used as complementary devices alongside batteries and fuel cells in applications which include hybrid electric vehicles (HEVs), power quality management and renewable energy.

ECs can be classified into electrical double-layer capacitors (EDLCs) and pseudo-capacitors (PCs) due to their charge storage mechanisms. EDLCs store charge electrostatically at electrode / electrolyte interface whereas PCs store energy by the fast and fully reversible redox reaction at the surface of the active electrode materials [3]. Carbon based materials such as graphene, carbon nano-tubes and activated carbons are commonly adopted electrode active materials in EDLCs [4, 5]. High specific surface area (SSA), good electrical conductivity, cost effectiveness and tailored porosity in accordance with the chosen electrolyte make activated carbon the most adopted electrode materials in ECs applications [6, 7]. In addition to electric double layer capacitance, capacitive performance of ECs cell can be further enhanced through pseudo-capacitive contribution by introducing the oxygen and nitrogen heteroatoms on the surface or into the carbon matrix. This improvement in capacitive performance of the EC cell is normally credited to the improved wettability (increases accessibility of the electrolyte ions to larger surface area) and higher electron conduction through the carbon matrix since certain nitrogen function groups have electron donor properties. In this work N- doped carbon and activated carbons were synthesised using sol-gel processes where nitrogen was incorporated into the bulk of the active material using melamine as nitrogen source. By enhancing the specific surface area and introducing the heteroatoms superior capacitive performance was achieved.

2 EXPERIMENTAL

2.1 Synthesis of MR/F and RF Aerogels

Nitrogen doped resorcinol (R) formaldehyde (F) aerogels gels were synthesized by polycondensation using sodium carbonate (C) as catalyst and melamine as a nitrogen source. For the preparation of melamine-resorcinol-formaldehyde (mRF) gels, RM solution was prepared by mixing the predetermine amount of resorcinol and melamine (M) in distilled water (W) at room temperature and the catalyst (C) was added. The solution was heated to 80 °C and mixed under vigorous stirring for 45 mins. The solution was cooled down and Formaldehyde (F) was added and kept on stirring for another 45 mins at room temperature. R/F and R/W (gml^{-1}) were kept constant at 0.5 (which is considered as the stoichiometric ratio) and 0.1 respectively whereas R / M ratio was kept at 80. The homogenous solution was placed in oven at 25 °C for 24 hrs to allow the gelation process to start in sealed glass vials by preventing the evaporation of water during the gelation. Temperature was increased to 60 °C for 72 hrs and finally temperature was increased to 80 °C for 48 hrs for the completion of the gelation process. Gels were immersed in acetone for solvent exchange to remove water from gel structure prior to vacuum drying. Finally, the gels were dried in a vacuum oven at 64 °C for 4 days.

2.2 Carbonization of mRF aerogels

Calcination of the dried mRF aerogels was performed at 800 °C for 3hrs to investigate the effect of pyrolysis conditions on the porous structure of carbon aerogels. The gel was placed in middle of tubular furnace using ceramic boat and purged with argon at room temperature for 30 mins prior to heating program. The furnace temperature was increased at 5 °C min^{-1} to 150 °C and maintained for 30 mins. It was further heated to 450 °C at 5 °C min^{-1} and held for 30 mins. Finally it was heated to the final pyrolysis temperature of 800 °C using the heating rate of 10 °C min^{-1} and kept for 3 hrs. After pyrolysis, the furnace was cooled under Ar flow to room temperature. All heating programs were performed using 3g of gel with Ar flow rate at 240 ml min^{-1} .

2.3 Activation of mRF aerogels

Activation of nitrogen doped carbon aerogels (mRFC) was performed under a CO₂ atmosphere in wide temperature range (750 - 900 °C) at different degrees of burn-off. Prior to heating, sample was placed in the centre of tubular furnace under the constant flow of Ar at 30 °C for 30 mins. The gas was switched from Ar to CO₂ once the desired activation temperature was achieved. Samples were kept under CO₂ flow for the time of activation followed by cooling down to room temperature under Ar.

2.4 Electrode preparation

For the fabrication of electrodes for EC cell in order to analyse the active material using electrochemical measurements, approximately 80 wt% active carbon material (well grinded powder), 10 wt% Cabot carbon black XC72 as conductivity enhancer and 10 wt% Kynar 2801as binder were used. The paste was then rolled into sheets and the thickness of the film was controlled using an applicator. Circular discs with diameter of 1.33 cm were then punched out from the films after overnight drying in a vacuum oven at 85 °C.

3 PHYSICAL CHARACTERIZATION OF CARBON AEROGELS

The porous structure of nitrogen doped carbon (mRFC) and nitrogen doped activated carbon (mRFCA) aerogels was characterized by a Tri-Star adsorption analyser (Micromeritics). The samples were evacuated in a vacuum oven at 80 °C at 5 mbar for 24 h followed by purging them in a nitrogen flow at 300 °C in a Flowprep system (Micromeritics) prior to the adsorption / desorption measurements. BET method was used for surface area measurements, t-plot method was used for micropore analysis, and BJH method using adsorption branch of the isotherm was used to calculate pore size distribution. The total pore volume was determined from the adsorbed volume of nitrogen at saturation pressure ($P/P_o = 0.99$) [8].

3.1 BET analysis mRFC and mRFCA

BET measurements were carried out to analysed the enhancement of the specific surface area and N₂ adsorption-desorption isotherms of N- doped carbon / activated carbon aerogels are shown in figure 1. It can

be seen that with the increase in activation temperature the volume of gas adsorbed increase which represents the development of porosity in the samples.

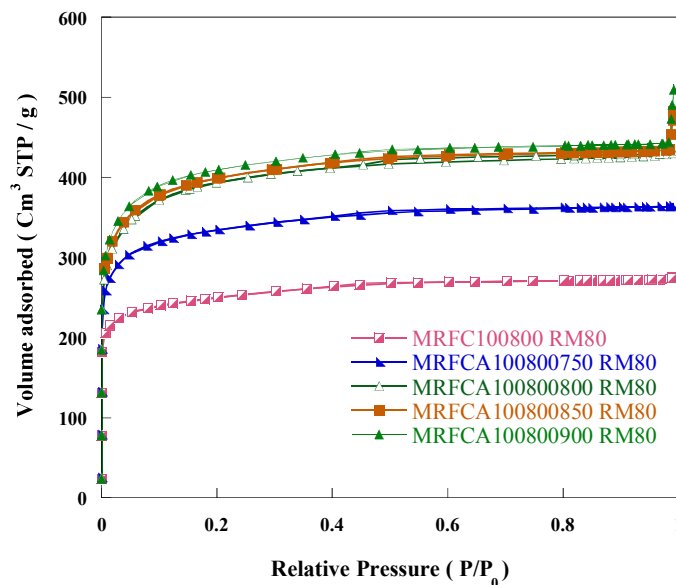


Figure 1 N₂ adsorption–desorption isotherms of N- doped carbon / activated carbon aerogels at different activation temperatures.

Figure 2 shows the pore distribution mRFC and mRFCA samples with the peaks around 2nm, which suggest the presence of both micropores and small mesopores.

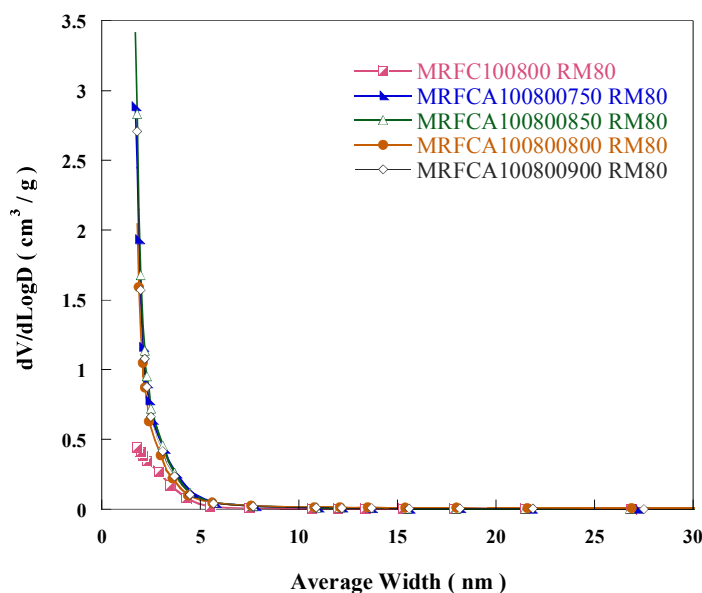


Figure 2 Pore size distribution N- doped carbon / activated carbons aerogels at different activation temperatures.

Specific surface area and pore characteristics for each sample derived from the isotherms are given in Table1. Results in Table 1 show that although there is a marked increase in specific surface area and total pore volume with increasing the activation temperature during thermal treatment, these materials have similar pore size distribution, which allows for comparisons between their capacitances to be made on the basis of a specific surface area and nitrogen content.

Table 1 Porosity parameters of nitrogen-doped carbons /activated carbons (at R/M 80) carbon aerogels

Sample	S_{BET} ($m^2 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{meso} ($cm^3 g^{-1}$)	V_{micro} %	V_{meso} %	D_{ave} (nm)
mRFC100800	841	0.4304	0.2833	0.1471	66	34	2.05
mRFCA100800750	1125	0.5680	0.3641	0.2039	64	36	2.02
mRFCA100800800	1333	0.6706	0.3762	0.2944	56	44	2.01
mRFCA100800850	1332	0.7464	0.3976	0.3488	53	47	2.24
mRFCA100800900	1372	0.7980	0.4243	0.3737	53	47	2.33

4.0 ELECTROCHEMICAL MEASUREMENTS

VoltaLab 40 radiometer analytical potentiostat was used to carry out electrochemical measurements. In order to stabilize the cell, it was kept under open circuit for 15 minutes prior to electrochemical measurements. Cyclic voltammetry (CV) measurements were used for the capacitance calculations with a voltage range between 0.5 and 1 V at scan rates of 5, 10, and 15 mVs⁻¹. Electro-chemical impedance spectroscopy (EIS) was also performed at the AC voltage amplitude of 10 mV and the frequency range of 100 KHz to 5 Hz with number of frequencies (per decade) of 5.

4.1 Electrochemical characterisation

Prior to the electrochemical measurements electrolyte was added to carbon electrode and placed in vacuum oven for 20 mins under modest vacuum level for enhanced penetration of electrolyte ions in porous structure of carbon. In this work 6 M KOH solutions was used as electrolyte in sandwich type symmetric capacitor cell.

Specific capacitance was calculated from the discharge curve of CV using the following equation;

$$C = \frac{I}{\left(\frac{dV}{dt}\right)} \quad (1)$$

Where I is the average discharge current and dV/dt is the scan rate. The specific capacitance C_{sp} in Fg⁻¹ was calculated by:

$$C_{sp} = 2 \times C/m \quad (2)$$

Where 'C' is the measured capacitance for two-electrode cell and m is the mass of active material in one electrode.

Figure 3 shows the cyclic voltammetry (CV) profile of the carbon samples which maintains a quasi-rectangular shape at all scan rates of 5, 10 and 15 mVs⁻¹, indicating the capacitive behaviour of all samples [9].

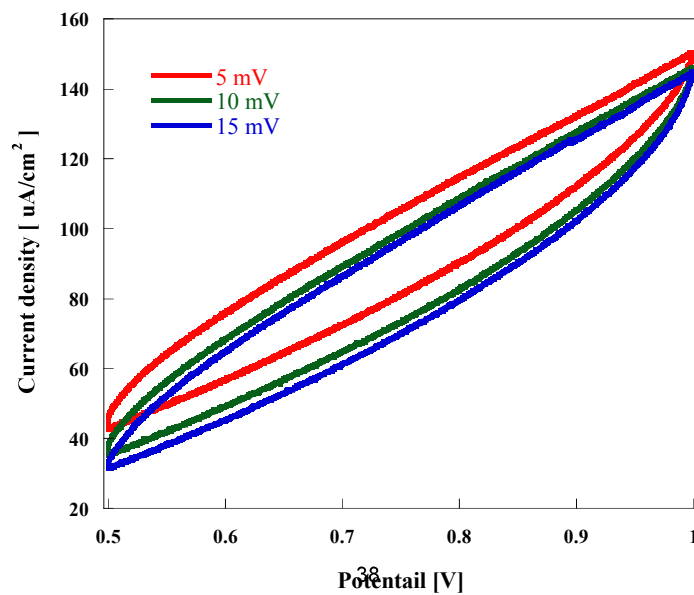


Figure 3 Cyclic Voltammogram of the cell using (mRFC100-800-800) N- doped activated carbon aerogel as the electroactive material at different scan rates

Table 2 Specific capacitance of the electrodes at different scan rate in 6M KOH electrolyte

Sample	Activation temperature ($^{\circ}\text{C}$)	Specific surface area (m^2g^{-1})	Specific Capacitance (Fg^{-1})		
			Scan rate (mVs^{-1})		
			5	10	15
mRFC100800	-----	841	208	70	19
mRFCA100800	750	1125	130	39	22
mRFCA100800	800	1333	289	75	31
mRFCA100800	850	1332	184	15	9
mRFCA100800	900	1372	162	60	35

Table 2 shows the specific capacitance values of nitrogen doped carbon (mRFC) and activated carbons (mRFCA). It is apparent that with increasing the activation temperature there is an improvement in the capacitive performance however increasing temperatures beyond 800°C results in drop in specific capacitance. Despite the increase in SSA there is drop in specific capacitance which can be down to increased meso-porosity and decrease in microporosity since microporosity contributes towards energy storage whereas meso-porosity assist in mobility of electrolyte ions through the active material.

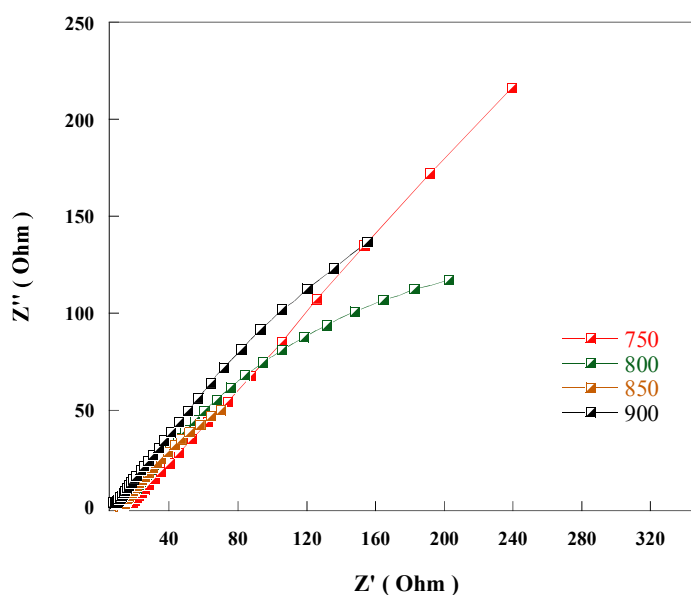


Figure 4 EIS spectra N- doped activated carbon aerogel with different activation temperature

Electrochemical impedance spectroscopy is employed to investigate the electrochemical behaviour of nitrogen doped electrode material. Figure 4 shows the Nyquist plots in 6 M KOH solution measured in the frequency range from 100 KHz to 50 Hz of nitrogen doped activated carbons, activated at different temperatures and degrees of burn off. EIS spectra consist of near vertical lines, an almost 45° diagonal line and very small semicircle [10, 11]. In low frequency range observation of these near vertical lines indicate the excellent electrochemical capacitive behaviour of all nitrogen doped samples when used as electrode in the cell [12]. The intermediate frequency region 45° line which represents ion diffusion and charge

Transportation into the electrode materials whereas semicircle relates to charge transfer resistance and polarization resistance where smaller diameter corresponds to faster kinetics.

CONCLUSIONS

Nitrogen doped carbon (mRFC) and activated carbons (mRFCA) were synthesised by polycondensation reaction in order to investigate the effect of activation on physical and electrochemical characteristics of electrode-active material. Porosity analysis displayed inconsequential change in pore size however enormous increase in specific surface area was observed. Electrochemical measurements established that physical activation and introduction of nitrogen functional groups can have a positive effect on specific capacitance of the cell. Specific capacitance was increased from 208 Fg⁻¹ to 289 Fg⁻¹ after activation. Increase in specific surface area and nitrogen content played a key role in improving capacitive performance of electrochemical cell. These results demonstrate that by improving the porous structure through physical activation using CO₂ and by introducing nitrogen functionalities into the carbon matrix, superior electrochemical performance can be achieved which makes nitrogen doped resorcinol/ formaldehyde based polymeric carbons a promising candidate to be adopted as electrode material for high performance electrochemical capacitor applications.

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